

Final Report

The Application of Magnesium(I) Compounds to Energy Storage Materials

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The Application of Magnesium(I) Compounds to Energy Storage Materials

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1. Objectives

The originally proposed objectives of this study centered on a further extension of preliminary results reported by the Principal Investigator Jones on the first examples of magnesium(I) compounds (*Science*, 2007, 318, 1754). Such species should not be seen as inaccessible or highly unstable targets. They are, however, very reactive, highly reducing and offer many potential applications to synthetic chemists, materials chemists, metallurgists and theoreticians. Accordingly, it was proposed to extend the prior and very successful AFOSR/AOARD funded study (FA8690814063) to a systematic exploration of the fundamental and applied chemistry of magnesium(I) and related, yet unknown, mixed valence magnesium clusters. Particular attention was to be paid to the use of such complexes in the preparation of energy storage materials. The deliverables the project was expected to produce in its one year span were:

- (i) to develop a variety of new β -diketiminate (and related ligand) coordinated magnesium(I) complexes of varying steric bulk, reactivity etc. N.B. Attempts were to be made to access the first examples of mixed valence magnesium clusters, L_nMg_m ($m > n$).
- (ii) to generate results related to the reversible addition of dihydrogen to magnesium(I) dimeric complexes, both in the presence and absence of catalysts.
- (iii) to produce data on the interaction of magnesium(I) complexes with other closely related hydrogen delivery systems, e.g. ammonia borane, $BH_3(NH_3)$ and other p-block metal hydride systems.
- (iv) to produce materials that have potential for use as explosives, propellants etc., using magnesium(I) dimers as critical reducing reagents. The demonstration of the latter in this respect, as reagents for N-N and other element-element bond forming reactions was expected to be achieved.

2. Abstract

This project has been extremely successful and good progress has been made towards all of the originally stated goals. Briefly, (i) several new β -diketiminate and guanidinate coordinated magnesium(I) dimers have been prepared and fully characterized. The ligands in these systems are of

varying steric bulk, thereby allowing for the facile tuning of the level of the reactivity of the dimers as reducing agents in further studies. (ii) A number of attempts have been made to prepare mixed valence magnesium(I) clusters, L_nMg_m ($m > n$), using both monodentate and bidentate ligands (L). Although, well defined systems have not been accessed, excellent progress has been made in this direction, which will be pursued in future studies. (iii) The addition of dihydrogen to Mg dimers has been achieved in the presence of a transition metal(0) complex. (iv) The preparation of a range of magnesium amino-borane complexes, $LMgNH_2.BH_3$ have been prepared and shown to decompose to generate H_2 at ca. 100 °C. (v) Magnesium(I) dimers have been demonstrated to be highly effective for the reductive coupling of alkyl azides to generate high N-content complexes which have potential as high energy materials. (vi) In a spin off study Mg dimers have been used as bespoke reagents to give high yields of Si^I , Ge^I and Sn^I dimers, and the first example of a germanium(I) radical, all of which are proving extremely reactive towards small molecule activations. The study as a whole has generated four papers (including 1 review article) in the period, with at least another four to be published in the next 12 months. PI Jones has delivered 8 invited lectures at conferences and institutions in four countries in the period.

3. Introduction

The chemistry of the main group elements has seen a remarkable resurgence of interest over the past decade. This renaissance has been driven by major breakthroughs in the development of methodologies to stabilize very low oxidation state and/or low coordination number p-block compounds that were previously thought incapable of existence under normal conditions. Although of great fundamental interest, in recent times these highly reactive species have begun to find applications in a variety of areas including catalysis, nano-chemistry etc. Despite the recent advancement of the low oxidation state chemistry of the p-block elements, there has been no similar progress in the s-block. This situation changed in 2007 when we published the syntheses of the first magnesium(I) complexes, $[(Priso)MgMg(Priso)]$ (Priso = guanidinate) and $[(Nacnac)MgMg(Nacnac)]$ (Nacnac = β -diketiminate). These compounds are remarkably thermally stable (dec. > 200 °C), and only moderately air and moisture sensitive. Accordingly, they have great potential as specialist, soluble reducing agents in synthesis, materials chemistry etc. This potential has been realized to some extent in very successful prior work carried out by us and funded by AFOSR/AOARD (FA8690814063).

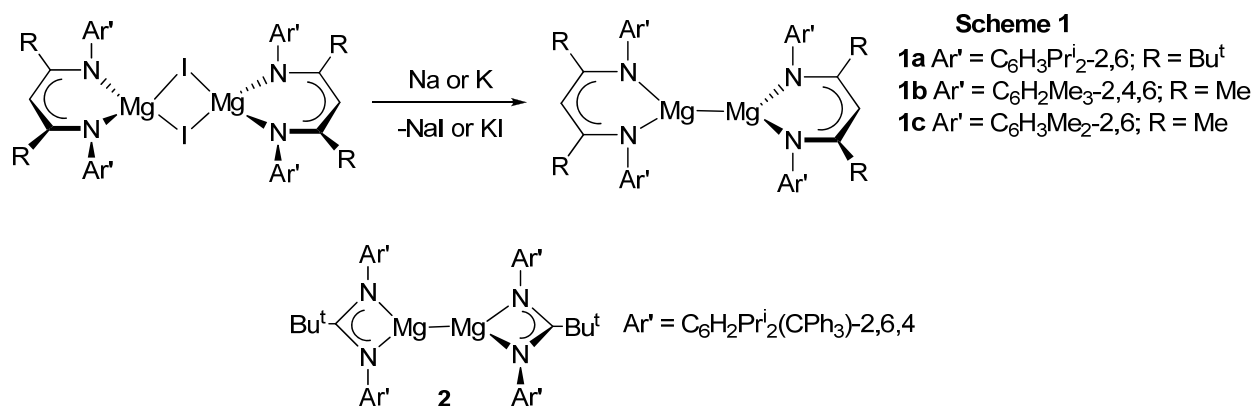
The general original objective of the current study was to systematically extend this work by exploiting our landmark magnesium(I) complexes for use in the preparation of novel energy storage materials, and experimental models of these systems (specific objectives are given above). The

originally proposed studies of the reversible addition of H_2 to magnesium(I) compounds, and the related activation of $BH_3(NH_3)$ towards H_2 loss by Mg^I and Mg hydrides, were thought to provide a unique opportunity to gain an understanding of the mechanisms of hydrogenation and dehydrogenation in MgH_2 and BH_3 based hydrogen storage systems. Such systems are widely used as hydrogen sources in fuel cell technology. Fuel cells are becoming increasingly important to the Air Force and other branches of the military for a number of reasons. They are used to power land based vehicles that are more economical, cleaner running and have a much reduced heat signature relative to internal combustion engine powered vehicles. Moreover, the high power to weight ratio of fuel cells is lending them to use as personal, light weight portable power supplies for military personnel in the field. In fact, as fuel cell technology advances, they will continue to replace more conventional batteries wherever they are used for military or other applications. It is clear, however, that significant advances need to be made in optimizing the efficiency, economy and rechargability of the hydrogen sources of fuel cells, before their use becomes widespread. With respect to the proposed work utilizing magnesium(I) compounds to economically prepare monomeric and polymeric hexazenes, the demonstrated high nitrogen/energy content of these materials could lead to their application as environmentally friendly, heavy metal free explosives, propellants and/or primers. This would benefit the Air Force through their potential application in munitions, missiles etc.

4. Experiment, Results and Discussion

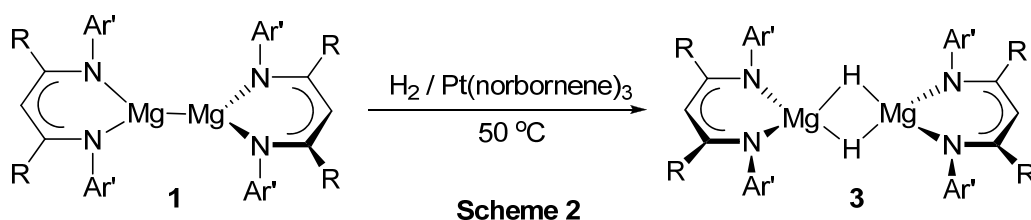
(i) β -Diketimate magnesium(I) complex development

In order to have on hand an array of magnesium(I) complexes of varying and tunable reactivity for the studies detailed below, a series of known and new β -diketimate ligands have been applied to the preparation of a variety of new magnesium dimers, e.g **1**, *via* the reduction of Mg^{II} precursor complexes (Scheme 1). These exhibit a wide range of reactivities from the very bulky system, **1a**, which, remarkably, is stable in the air for up to 1 hour, to the least hindered system, **1c**, which spontaneously combusts in air, yet is stable indefinitely under a dinitrogen atmosphere at ambient temperature. In unpublished work we have also prepared the first example of an amidinate stabilized Mg^I system, **2**, the reactivity of which is being compared to that of **1** in further studies. Moreover, progress has been made towards the preparation of mixed valence Mg cluster compounds, L_nMg_m ($m > n$) ($L = \beta$ -diketimate or bulky amide), *via* co-reductions of $MgI_2/LMgI$ mixtures with alkali metals. Although no such clusters have been structurally characterized, this is a goal of follow-on work.



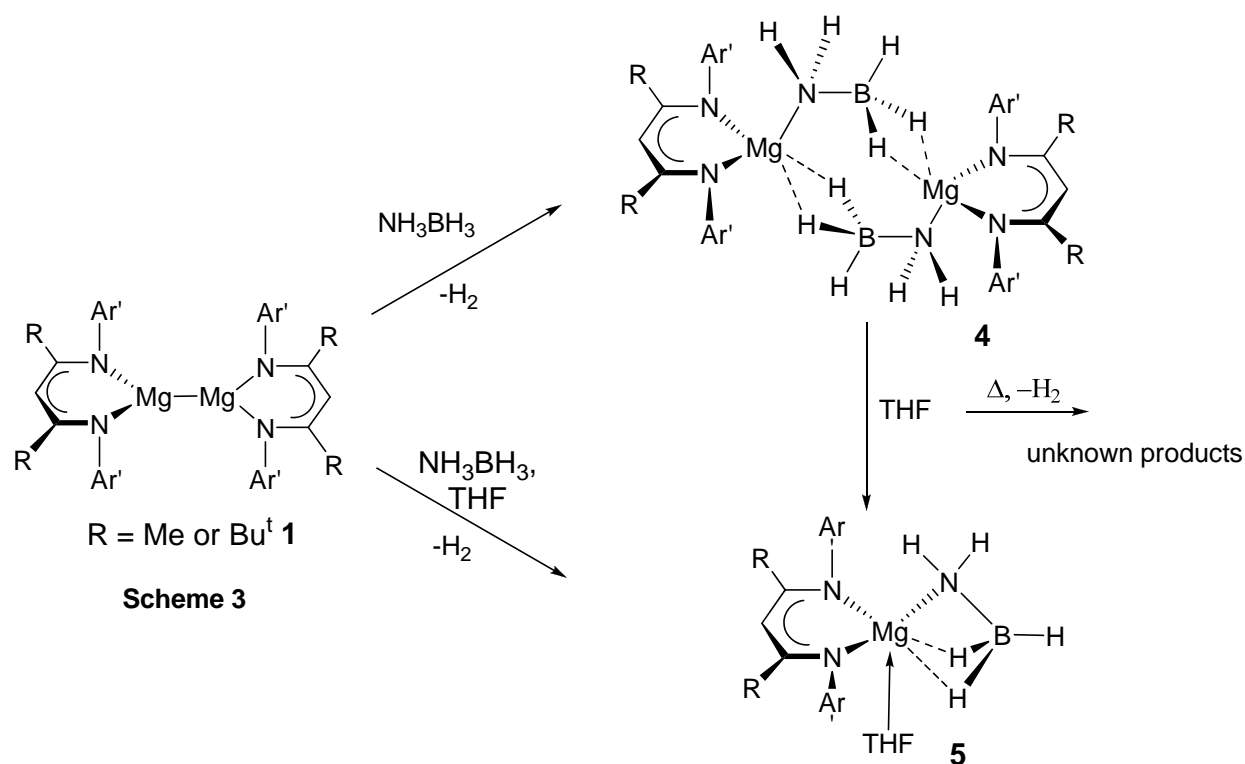
(ii) Magnesium(I) complexes for the study and optimization of hydrogen storage systems

In this phase of the project, the use of β -diketiminate magnesium(I) complexes as soluble models for the reversible addition of dihydrogen to magnesium metal has begun to be investigated. The Mg/MgH₂ system has a high hydrogen content (7.6% w/w) and can store significantly more hydrogen (v/v) than liquified dihydrogen. However, high temperatures (> 300 °C) are required for both its dehydrogenation and rehydrogenation. This problem has been overcome to some extent in the past by the incorporation of p-block or transition metals into the system (e.g. Al, Ti, V, Fe, Co, Ni or Cr). However, little is known of the mechanisms by which these metals improve the kinetics of the hydrogenation/dehydrogenation of the Mg/MgH₂ system. We have utilized compounds **1** as soluble models of this system in an attempt to shed light on this problem. Preliminary studies in this direction have been successful in that while **1** does not react with H₂ to any great extent under ambient conditions, the presence of small amounts (*ca.* 5 mol%) of the platinum(0) complex, [Pt(norbornene)₃], in the reaction mixture cleanly catalyzes this reaction (Scheme 2). Presumably an intermediate platinum(II) hydride complex is formed which is subsequently dehydrogenated by the highly reducing Mg^I compound to give the Mg^{II} hydride systems, **3**. Further studies to elucidate the mechanism of this catalytic reaction are in hand. The results of this work will be of much interest to researchers involved in optimizing the hydrogen storage capacity, kinetics and multiple hydrogen sorption/desorption cycling capabilities of the MgH₂/Mg system. It is of note that we have also carried out the formal hydrogenation of **1** through its reaction with an N-heterocyclic carbene (NHC) adduct of AlH₃, as a hydrogen source. This led to **3**, and an unprecedented NHC adduct of the parent dialane(4), *viz.* [(NHC)Al(H)₂Al(H)₂(NHC)]. A publication has appeared on this work (*Nature Chem.*, 2010, **2**, 865).



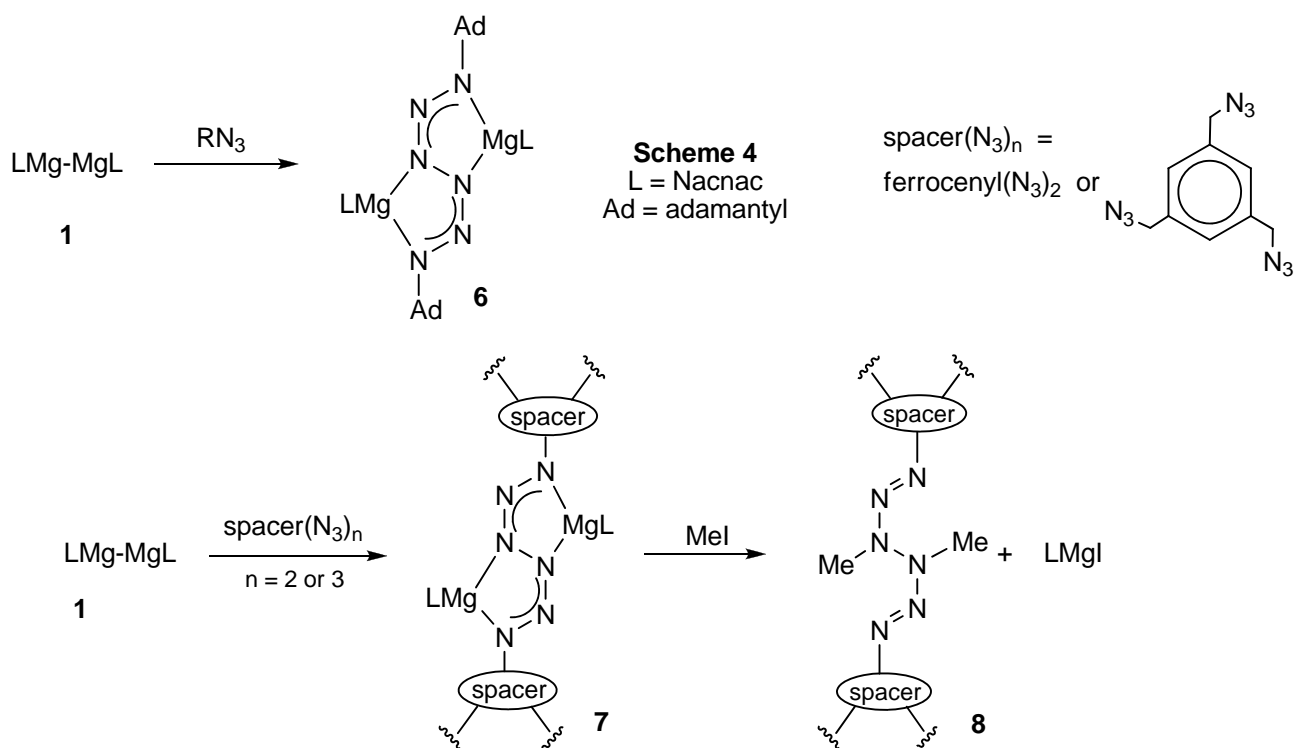
In a related arm of this study the ability of magnesium(I) and magnesium(II) hydride complexes to activate ammonia borane (AB), $\text{BH}_3(\text{NH}_3)$, towards H_2 loss has been explored. Ammonia borane has been intensely studied in recent years due to its very high hydrogen content (19.6% w/w, i.e. far exceeding the DOE 2015 target of 9.0% w/w) and concomitant potential for use as a hydrogen storage system. Like MgH_2 , it too has a number of problems in this respect. Firstly, it can theoretically release three equivalents of H_2 per molecule of AB, but in practice the release of only two molecules is feasible, and even this requires high temperatures ($> 200\text{ }^\circ\text{C}$). Furthermore, another downside of the process is that it yields a variety of oligomeric/polymeric products of the type $(\text{HBNH})_n$, which include toxic borazine ($n = 3$). However, a number of transition and s-block metal catalysts have been shown to reduce the temperature, and enhance the kinetics, of H_2 release from AB. For example, CaH_2 reacts with AB to give $\text{Ca}(\text{NH}_2\text{BH}_3)_2$ which can release its hydrogen at much lower temperatures (*ca.* $120\text{ }^\circ\text{C}$) than AB, without the problematic generation of borazine. Interestingly, a similar reaction between AB and MgH_2 does not occur. However, if $\text{Mg}(\text{NH}_2\text{BH}_3)_2$ could be accessed, it would have the distinct advantage over $\text{Ca}(\text{NH}_2\text{BH}_3)_2$, in that its hydrogen content is significantly higher (11.9% vs. 10% w/w).

In preliminary work, and later during the project period, we have shown that β -diketiminato magnesium(I) and magnesium(II) hydride complexes readily react with AB at $0\text{ }^\circ\text{C}$ to give the dimeric magnesium amide complexes, **4**, *via* hydrogen loss (Scheme 3). Treating this with THF leads to the monomeric systems, **5**. Depending on the steric bulk of the β -diketiminato ligand, compounds **4** eliminate 1 equiv. of H_2 slowly at $40\text{ }^\circ\text{C}$, increasing to rapidly at temperatures of approx. $100\text{ }^\circ\text{C}$. We have explored the nature of the by-products of these dehydrogenation reactions (which do not include borazine), and the reversibility of the dehydrogenations with limited success to date. Efforts continue in this area of the study and a publication has been submitted on this work.



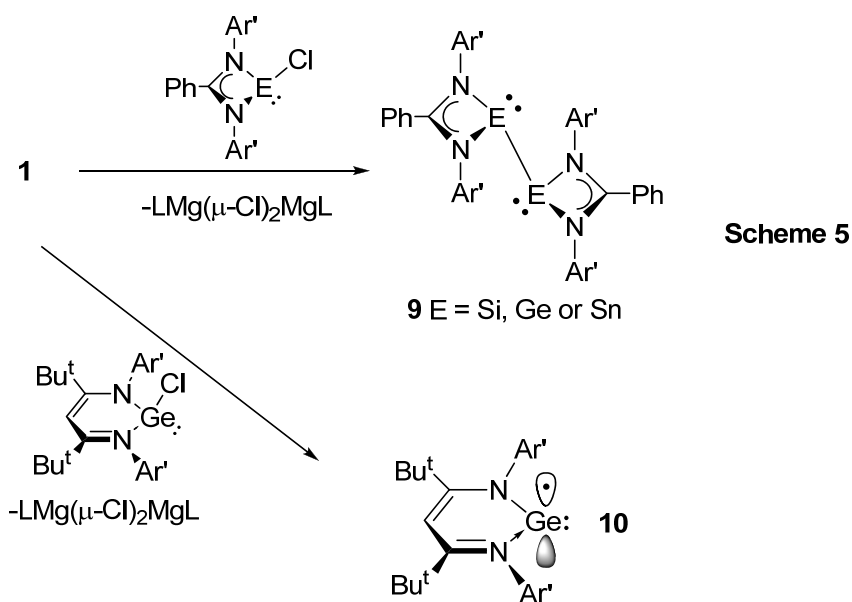
(iii) Magnesium(I) complexes in the synthesis of high energy/high N-content materials

The originally proposed goal of accessing a range of magnesio-hexazenyl systems, **6**, has been successful and several new systems with variable steric bulk of the β -diketiminato ligand have been prepared (Scheme 4). Some aspects of this work has been published (*Chem. Eur. J.*, 2010, **16**, 938). In addition, reactions of magnesium(I) compounds with polyfunctional azides have been carried out and these have afforded insoluble materials which spectroscopic evidence suggests are **7**. Initial experiments to quench these systems with electrophiles, e.g. MeI, yield organic materials which initial characterization suggests are polymers resembling, **8**. In collaboration with polymer chemists at Monash, work is ongoing to fully characterize these materials.



(iv) Magnesium(I) complexes as specialist reducing agents in p-block chemistry

As an important spin-off of this study, we have found that magnesium(I) compounds act as very facile and selective reducing agents in the formation of low oxidation state group 14 systems that are inaccessible using more traditional reducing agents such as alkali metals. Some initial work has been published in two high profile papers (*Inorg. Chem.* (Forum Article), in press; *J. Am. Chem. Soc.*, 2011, **133**, 10074). This study has yielded, for example, the first high yielding routes to the element(I) dimers, **9**, and the first example of a monomeric germanium(I) radical, **10** (Scheme 5). Remarkably, the latter is indefinitely stable in the solid state and has been fully characterized using EPR/ENDOR spectroscopies, X-ray crystallography and computational analyses. These and related compounds prepared in the study are very reactive towards activation of a range of small molecules, e.g. H_2 , NH_3 , CO , C_2H_4 , CO_2 etc. In the last year this has become a focus of our research and we are exploring the reversibility of such activations. If this can be achieved, such compounds hold considerable potential for the replacement of transition metal based systems in a range of stoichiometric and catalytic synthetic transformations.



5. Personnel Supported

Other than myself as Principal Investigator, a number of personnel within the group have received direct support from the contract and/or were associated with the project. Two PhD students, Mr. Simon Bonyhady and Mr. William Woodul received support from the contract and have been involved in many aspects of the work. Another graduate students, Mr. Sam Lim Choong, although not stipend supported, has been involved in the azide coupling aspects of the study and continues to pursue these as part of his PhD work. Dr. Sharanappa Nembenna has contributed to the programme as a synthetic technician, though his expertise in NMR spectroscopy and group 2 chemistry have also been invaluable to the project. Mr. Brant Maitland was employed as a part time technician and has been involved in the routine ligand and starting material preparations etc.

It should be noted that I have instigated a large number of international collaborations as a direct result of this project. These include interactions with theoreticians, Frenking (Marburg, Germany) and Kaupp (Berlin, Germany); an EPR/ENDOR spectroscopist, (Murphy, Cardiff, UK); a neutron diffraction X-ray crystallographer (Edwards, Sydney, Australia), an experimental charge density crystallographer (Overgaard, Denmark); and an electrochemist, Hartl (Reading, UK). The input from these collaborators has been invaluable and will continue into the future.

6. Publications

The following publications resulted from the project and appeared during the contract period and acknowledge AFOSR/AOARD support (see attached reprints):

1. Invited Forum Article: The Preparation, Characterization and Theoretical Analysis of Group 14 Element(I) Dimers: A Case Study of Magnesium(I) Compounds as Reducing Agents in Inorganic Synthesis, C. Jones, S.J. Bonyhady, N. Holzmann, G. Frenking and A. Stasch, *Inorg. Chem.*, in press.
2. A Neutral, Monomeric Germanium(I) Radical, W.D. Woodul, E. Carter, R. Müller, A.F. Richards, A. Stasch, M. Kaupp, D.M. Murphy, M. Driess and C. Jones, *J. Am. Chem. Soc.*, 2011, **133**, 10074-10077.
3. β -Diketiminato Stabilized Magnesium(I) Dimers and Magnesium(II) Hydride Complexes: Synthesis, Adduct Formation and Reactivity Studies, S.J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A.J. Edwards, G.J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938-955.
4. A. Stasch and C. Jones, Stable Dimeric Magnesium(I) Compounds: From Chemical Landmarks to Versatile Reagents, *Dalton Trans.* (Perspective Article), 2011, **40**, 5659-5672.

In addition, one paper has been submitted which details aspects of the work on magnesium(I) compounds and their reaction with ammonia borane

5. Facile dehydrogenation of ammonia borane with magnesium(I) dimers and magnesium(II) hydride complexes, S.J. Bonyhady, S. Nembenna, A. Stasch and C. Jones, *Eur. J. Inorg. Chem.*, submitted.

7. Interactions

The results generated from the contract have formed a major component of the invited lectures at international conferences and institutions as detailed below:

1. "Molecular Magnesium(I) Compounds: From Chemical Landmarks to Versatile Reagents", Invited lecture for the special symposium "Commemoration of the founding of the ACS journal Organometallics", ACS National Meeting, Boston, August, 2010.

2. "Molecular Magnesium(I) Compounds: From Chemical Landmarks to Bespoke Reagents for Synthesis", Invited Windows on Science lecture at the US Air Force Office of Scientific Research contractors review meeting, Washington DC, September, 2010.
3. "Molecular Magnesium(I) Compounds: From Chemical Landmarks to Versatile Reagents", Invited session lecture, Pacifichem, Hawaii, December, 2010.
4. "Group 2 and 13 Metal(I) Heterocycles: Fundamentally Appealing yet Functional Compounds", Invited session lecture, Pacifichem, Hawaii, December, 2010.
5. "Molecular Magnesium(I) Compounds: "Bespoke" Reducing Agents for the Synthetic Chemist", UC Davis, Department of Chemistry, USA, June, 2011.
6. "Molecular Magnesium(I) Compounds: "Bespoke" Reducing Agents for the Synthetic Chemist", Invited Keynote Session lecture, Canadian Society of Chemistry, National Meeting, Montreal, Canada, June, 2011.
7. "Molecular Magnesium(I) Compounds: "Bespoke" Reducing Agents for the Synthetic Chemist", Invited lecture of the Unifying Concepts in Catalysis Excellence Cluster, TU Berlin, Germany, June, 2011.
8. "Molecular Magnesium(I) Compounds: "Bespoke" Reducing Agents for the Synthetic Chemist", Nanyang Technological University, Department of Chemistry, Singapore, June, 2011.

8. New

(a) No discoveries, inventions, or patent disclosures have yet resulted from the contract

(b) See attached **"DD Form 882, Report of Inventions and Subcontractors."**

9. Archival Documentation

Please see attached four reprints detailing aspects of the work carried out in this study.